

AGGREGATION OF THE NEODYMIUM COMPLEXES OF HDEHP, CYANEX 272, CYANEX 302, AND CYANEX 301 IN TOLUENE

M. P. JENSEN,^{1,*} R. CHIARIZIA,¹ V. URBAN,^{2,3} and K. L. NASH¹

¹Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439 USA

²IPNS Division, Argonne National Laboratory, Argonne, Illinois 60439 USA

³Present address: European Synchrotron Radiation Facility, F-38043 Grenoble, France

* Fax: 1-630-252-7501, e-mail: mjensen@anl.gov

Visible absorption spectroscopy and small-angle neutron scattering have been used to study the morphology and aggregation of a series of purified acidic organophosphorus extractants with oxygen and sulfur donor atoms and the Nd(III) complexes of these extractants in toluene solutions. The extractants bis(2-ethylhexyl)phosphoric acid (HDEHP), bis(2,4,4-trimethylpentyl)phosphinic acid (HC272), bis(2,4,4-trimethylpentyl)monothiophosphinic acid (HC302), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HC301) were studied. The phosphinic acid based extractants are the primary constituents of the commercial extractants Cyanex 272, Cyanex 302, and Cyanex 301 respectively. Small-angle neutron scattering experiments show that although 0.10 M solutions of the oxygen containing extractants HDEHP and HC302 are dimeric in toluene, HC301, which contains only sulfur donor atoms, is monomeric within the uncertainty of the experiment. When high concentrations of Nd (greater than 30% theoretical Nd capacity) are extracted into the organic phases, the oxygen containing extractants, HDEHP, HC272, and HC302 all form dinuclear complexes with a 2:6 metal:extractant ratio. The sulfur bearing extractant HC301, on the other hand, forms only 1:3 metal:extractant complexes when the Nd loading is less than 50% of the theoretical capacity of the solution. However, at higher Nd loading, 86% of the theoretical capacity, 2:6 Nd:C301 complexes are formed.

Key words: Solvent Extraction, Neodymium, Cyanex, Aggregation, Small-angle neutron scattering

1. INTRODUCTION

The chemistry of lanthanide and actinide cations with acidic organodioxophosphorus extractants like the dialkylphosphoric, -phosphonic, and -phosphinic acids has been well established by numerous studies of the tracer and macro scale extraction equilibria,[1] the coordination chemistry,[2-4] and even crystallization [5-7] of *f*-element-extractant complexes. The related acidic organophosphorus acid extractants that contain sulfur donors rather than oxygen donors are of interest for separating trivalent lanthanide and actinide cations. While the extraction equilibria of certain organo monothio- and dithiophosphorus extractants have been studied,[8-14] there is comparatively little information on the metal coordination or molecular structural of these sulfur containing complexes in organic solutions.

Fundamental studies of these extractants are important for developing useful separations processes, but the laboratory-scale studies are typically performed at low metal ion concentrations to discourage the formation of polynuclear aggregates in the organic phase. Industrial scale solvent extraction processes, on the other hand, usually are operated under conditions of high metal loading (i.e. high metal concentrations relative to the theoretical metal ion capacity of the extractant solution), which tends to promote the formation of polynuclear species. This work reports on the aggregation and morphology of a series of Nd³⁺ complexes at high metal loading in toluene with acidic organophosphorus extractants containing either two oxygen, one oxygen and one sulfur, or two sulfur donor atoms per extractant. The variation of the number of oxygen atoms attached to the phosphorus atom alters the acidity and hydrogen bonding characteristics of each extractant. In dilute metal ion solutions, this gives the *f*-ion complexes of dioxo, monothio, and dithio extractants different structures and stoichiometries. Three of the ligands studied (Fig. 1) are the major components

(75-90% [15]) of commercially available dialkylphosphinic acid based extractants intended for industrial scale processes: Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid, HC272), Cyanex 302 (bis(2,2,4-trimethylpentyl)monothio phosphinic acid, HC302), and Cyanex 301 (bis(2,4,4-trimethylpentyl)-dithiophosphinic acid, HC301). The other extractant, bis(2-ethylhexyl)phosphoric acid or HDEHP, is the most extensively studied organophosphoric acid extractant. It is used for industrial scale intra-lanthanide separations.

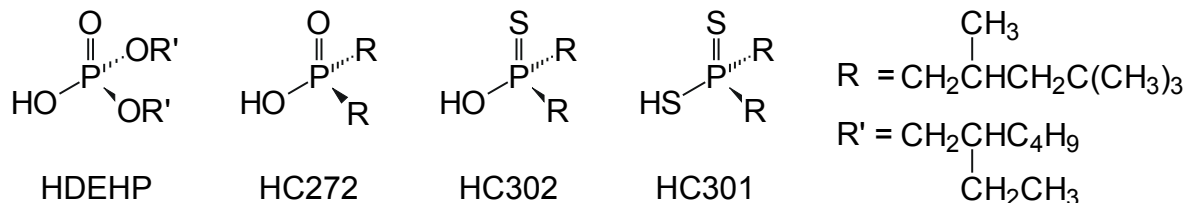


Fig. 1. Ligands used in this study

2. EXPERIMENTAL

Purification of the extractants, as described previously,[8, 16] resulted in purities of HDEHP: 99+%, HC272: 99%, HC302: 97%, and HC301: 99% as determined by ^1H and ^{31}P NMR. The extractants were dissolved in deuterotoluene (toluene- d_8 99 atom% D, Aldrich) to give 0.10 M solutions, except for HC272. The HC272 samples were not suitable for neutron scattering measurements because the maximum metal loading that could be achieved before the onset of precipitation was only 8% of the theoretical Nd loading capacity. (The theoretical Nd loading capacity is the maximum amount of Nd that would be present in the organic phase assuming that all of the extractant is present as Nd complexes with a 1:3 metal:extractant ratio). Therefore, HC272 was dissolved in normal, non-deuterated toluene (99.9%, Aldrich) for use in the spectrophotometric measurements. The organic phases were loaded with Nd by two phase titrations of aqueous 0.0337 M $\text{Nd}(\text{ClO}_4)_3/0.10$ M extractant in toluene with 1 M NaOH. Volume ratios of the organic to aqueous phases of 1.0 or 2.0 were used to vary the metal loading. Precipitates of the Nd-extractant complexes could be avoided if the NaOH titrant was added slowly in small increments. The concentration of Nd in the aqueous phases was determined by ICP-AES, and the organic phase Nd concentrations were calculated from the differences between the initial and final amount of Nd in the aqueous phases.

Small-angle neutron scattering (SANS) measurements on the HDEHP, HC302, and HC301 samples with and without Nd were made at the Argonne National Laboratory Intense Pulsed Neutron Source's time-of-flight Small-Angle Diffractometer, which was calibrated to give absolute scattering intensities. The instrument and data collection procedures have been described previously.[17-19] The SANS measurements were made at 22 ± 2 °C. The absorption spectra of the organic phases in 1.000 cm quartz cuvettes were measured from 350 to 850 nm using a modified Cary-14 spectrophotometer (OLIS, Inc.) at a fixed bandwidth of 0.06 nm and 25 °C. Fuller descriptions of the experimental conditions can be found in the literature.[20]

3. RESULTS

The results of a Guinier analysis [21] of the SANS data sets are summarized in Table I and Fig. 2. The neutrons are scattered most strongly by hydrogen atoms, which, in this case, are part of the extractant molecules. The presence of Nd, a comparatively poor neutron scatterer, is only observed indirectly, by its effect on the assembly of the small extractant molecules into larger coordination complexes. Although Nd cations promote the assembly of extractant

molecules into larger groups, none of the data sets show the telltale signs of large aggregates (aggregates composed of 20 or more monomers), increasing scattering intensity, $I(Q)$, for low values of Q , the momentum transfer.

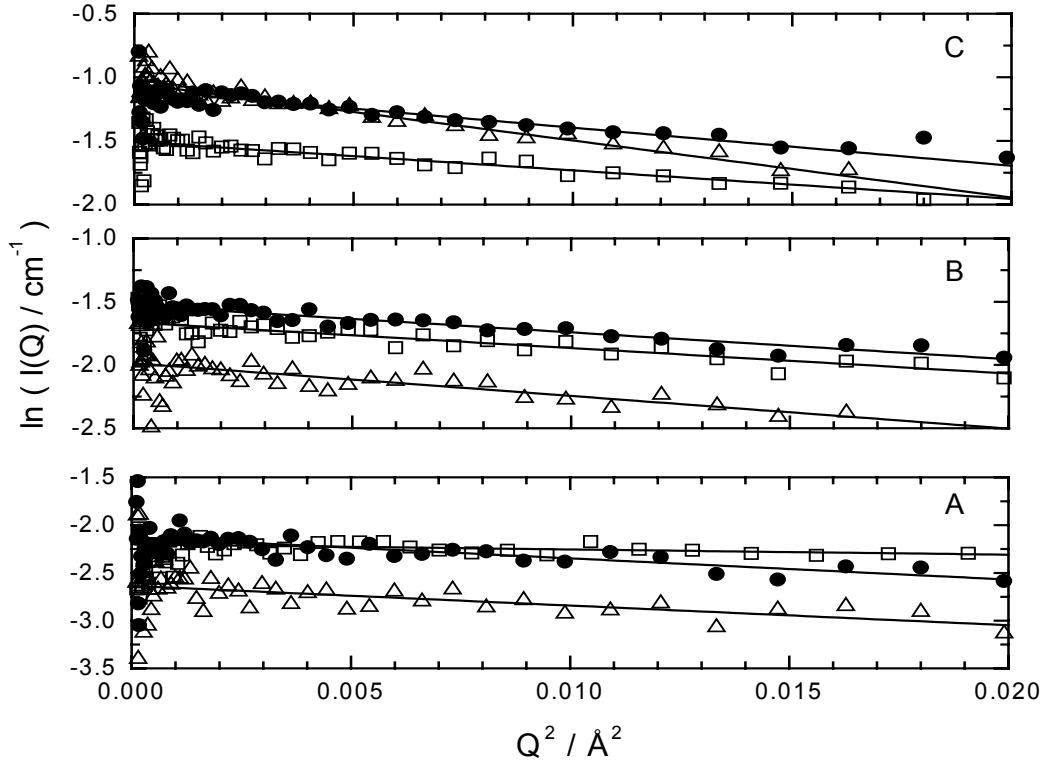


Fig. 2. Guinier plot of SANS data for (A) extractants only, (B) each extractant with lowest Nd loading, (C) each extractant with highest Nd loading, (\square) HDEHP, (\bullet) HC302, (Δ) HC301, and (—) linear least-squares fit.

The slope obtained from the Guinier analysis (when $QR_g \leq 1$) can be used to calculate the radius of gyration, R_g , which is a measure of the average spatial extension of the particles in the solution. The radius of gyration is the root-mean-squared distance of each atom in a particle from the center of gravity of the particle. This means that the geometric radius, diameter, or length of a given particle depends on the shape of the particle. For a spherical particle, for example, the actual geometric radius, R , is $(5/3)^{1/2} R_g$. The gyration radii increase when Nd is extracted into the solutions (Table I), demonstrating through simple geometry that the monomeric and dimeric molecules of extractant, which exist in the absence of the metal cations, are converted into larger, metal bound aggregates in the presence of Nd.

The magnitude and variation in the gyration radii suggest the presence of small aggregates in the solutions. The y-intercepts, $\ln I(0)$, derived from the Guinier analysis can be used to calculate n_w , the weight average aggregation number of the extractant molecules in the scattering particles, using the equation

$$n_w = \frac{6.022 \times 10^{26} d_{HL} I(0)}{[L]_{total} \Delta \rho^2 M W_{HL}^2} = \frac{\sum n^2 [(HL)_n]}{[L]_{total}},$$

where d_{HL} is the density of the undiluted extractant, $[L]_{total}$ is the total extractant concentration, $\Delta\rho$ is the difference of the scattering length densities of the extractant and solvent, and MW_{HL} is the molecular weight of the extractant.[18, 19]

Table I. Results of the Guinier analysis of the SANS data of the 0.10 M extractant solutions

HL	% Theoretical Nd Capacity	$\frac{[HL]}{[Nd]}$	R_g (Å)	n_w	Best n_w calc.	Modeled Nd Species
HDEHP	0		5.8 ± 1.7	2.0 ± 0.2		
	33	9.0	8.5 ± 0.6	3.3 ± 0.3	3.30	$Nd_2(DEHP)_6$
	36	8.2	8.0 ± 0.6	3.9 ± 0.3	3.43	$Nd_2(DEHP)_6$
HC302	0		9.2 ± 1.0	2.0 ± 0.2		
	48	6.3	8.2 ± 0.6	3.5 ± 0.3	3.89	$Nd_2(C302)_6$
	90	3.3	9.4 ± 0.4	5.3 ± 0.4	5.59	$Nd_2(C302)_6$
HC301	0		9.3 ± 0.6	1.07 ± 0.09		
	46	6.5	8.5 ± 1.0	2.0 ± 0.2	1.99	$Nd(C301)_3$
	86	3.5	11.9 ± 0.4	5.2 ± 0.4	5.33	$Nd_2(C301)_6$

All of the extractant species in the solution contribute to n_w and because each solution contains at least some uncomplexed extractant, the number of extractant monomers present in the Nd complexes cannot be directly derived from the aggregation numbers presented in Table I. However, the contribution of each species to n_w is directly proportional to its fraction of the total extractant concentration in the solution. Each n -mer of extractant, $(HL)_n$, which may or may not also contain Nd, contributes $n^2[(HL)_n]/[L]_{total}$ to n_w . This provides a mechanism to determine the predominant Nd species present even when there is a significant concentration of uncomplexed extractant. Assuming that $Nd(OH)_x^{3-x}$ or $Nd(ClO_4)_y^{3-y}$ complexes are not extracted under the conditions of the experiment, least-squares minimization of the n_w value calculated from a wide variety of integral Nd:extractant stoichiometries (Nd_mL_ℓ $m = 1,2,3$; $\ell = 3,4,5,6,9$) should give the most probable formula of the predominant species. The best calculated n_w values and the corresponding Nd complexes are also summarized in Table I.

Only small concentrations of Nd could be dissolved in 0.10 M solutions of HC272 before a precipitate began to form. HDEHP, which could be loaded to ca. 35% of the theoretical Nd capacity under these conditions, was used for the SANS studies instead, assuming that the coordination and aggregation of the two dioxo extractants is similar. To support this assumption, the Nd coordination environment in the HC272 and HDEHP complexes was compared by visible absorption spectroscopy. The f - f transitions of Nd complexes are very sensitive to the coordination environment. The spectra of HDEHP and HC272 solutions between 500 and 625 nm are shown in Fig. 3 for solutions near each extractant's maximum Nd loading, and also for a HDEHP solution with low Nd loading. The spectra measured near the highest achievable Nd loading are indistinguishable, which indicates a similar coordination environment, i.e. Nd_2L_6 , for both complexes. The intensity of the absorption bands are significantly lower for the Nd-HDEHP complex at high extractant concentration (1.5 M) and low Nd loading (3%), indicating the presence of a different complex.

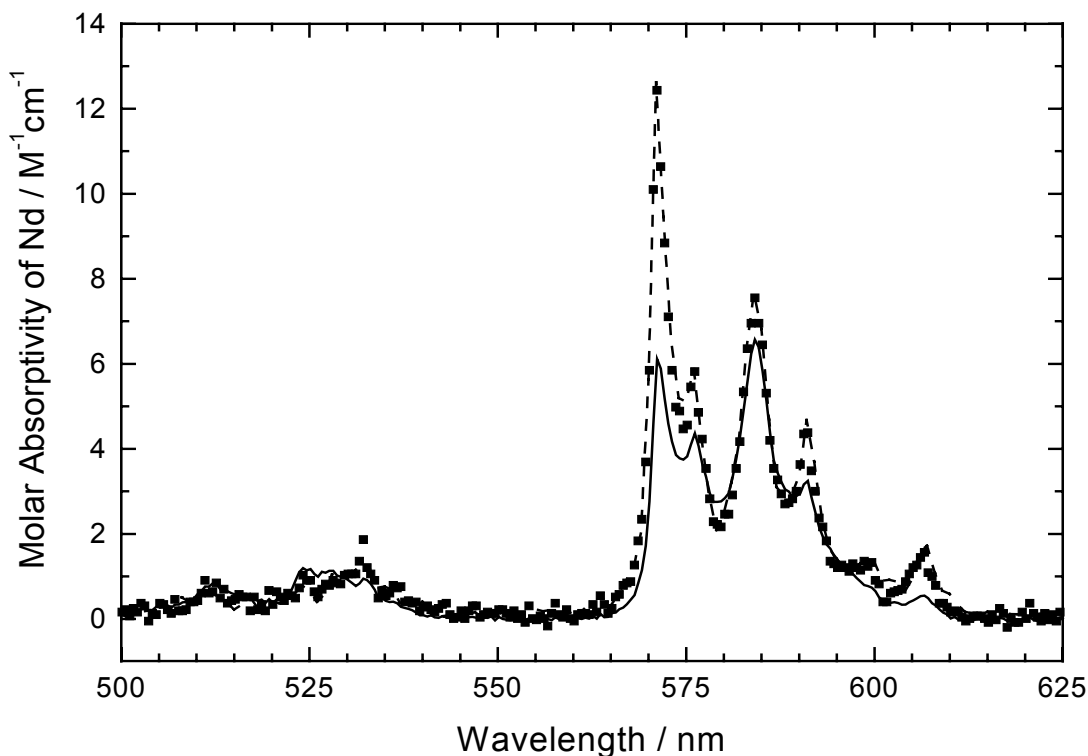


Fig. 3. Hypersensitive $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transitions for the Nd^{3+} complexes of HDEHP and HC272, (—) low (3%) Nd loading of 1.5 M HDEHP in dodecane, (- -) high (8%) Nd loading of 0.10 M HC272 in toluene, and (■) high (33%) Nd loading of 0.10 M HDEHP in toluene.

4. DISCUSSION

The properties of the unpurified, commercial grade Cyanex extractants have been reported in the literature previously. Vapor phase osmometry has demonstrated that HC272 and HC302 exist primarily as dimeric species, $(HL)_2$, in non-polar organic solvents in the absence of metal ions, while the results of a variety of techniques have shown that dithiophosphinic and dithiophosphoric acids related to HC301 are primarily monomeric at concentrations below ca. 0.2 M.[22] These findings are completely corroborated by the SANS measurements presented here. At extractant concentrations of 0.10 M in deuterated toluene, the oxygen containing extractants exist as $(HDEHP)_2$ and $(HC302)_2$ ($n_w = 2.0 \pm 0.2$). In contrast, HC301, which does not contain any oxygen can be considered monomeric within the experimental uncertainty of the measurement ($n_w = 1.07 \pm 0.09$). The S-H \cdots S hydrogen bonds required to form dimers of HC301 are much weaker than the O-H \cdots O and S-H \cdots O bonds found in $(HDEHP)_2$ and $(HC302)_2$. [23] They are too weak to promote dimerization of HC301 under these conditions.

The combination of the SANS data and the visible absorption spectra provide unequivocal evidence of the formation of dinuclear 2:6 (Nd:extractant) complexes for each of the extractants under certain conditions. The average aggregation number calculated for Nd_2L_6 (Table I) gives the best agreement with the measured aggregation numbers for all of the Nd containing solutions except for the HC301 solution at low loading (46% theoretical capacity). In this case, the 1:3 complex $Nd(C301)_3$ is superior at reproducing the measured value of n_w , which is 2.04 (calculated $n_w = 1.99$). As an example of the superiority of $Nd(C301)_3$ in

reproducing the measured aggregation number, the hypothetical complex $\text{Nd}(\text{C301})_3(\text{HC301})$ in the 46% Nd loaded HC301 solution gives a calculated $n_w = 2.90$, while the dinuclear complex $\text{Nd}_2(\text{C301})_6$ gives a calculated $n_w = 3.39$. Other Nd:L stoichiometries were even worse at reproducing the measured aggregation number.

The presence of 1:3 and 2:6 Nd:L complexes in the organic phases agrees with the known structural chemistry of dithiophosphinate and monothiophosphinate complexes. Crystal structures of discrete 1:3 and 1:4 R_2PS_2^- complexes of trivalent lanthanide cations have been reported in which steric constraints force the smaller trans-Nd lanthanide cations to form only the 1:3 complex with bis(cyclohexano)dithiophosphinic acid,[24] while Nd crystallized both as 1:3 and as 1:4 complexes. Both mononuclear 1:2 and dinuclear 2:4 M:L complexes of dithiophosphinic acid ligands with divalent *d*-transition metal cations have also been known for some time. The metal centers of the 2:4 complexes are bridged by two dithiophosphinate ligands, and each metal center is capped with an additional bidentate R_2PS_2^- ligand.[25, 26] Similar structures for *d*-transition metal complexes of phosphinic and monothiophosphinic acid ligands are also known. The dinuclear lanthanide complexes of bis(methyl)-monothiophosphinic acid have also been studied by x-ray crystallography,[27, 28] and several different structures, with and without bridging sulfur atoms, were observed.

The Nd_2L_6 stoichiometry reproduces the values of n_w better than any other single species for the extractants that contain at least one oxygen atom, HDEHP and HC302. However, the calculated n_w values of the 2:6 Nd:C302 complexes are both modestly larger than the experimentally determined values, suggesting that smaller amounts of other species, possibly $\text{Nd}(\text{C302})_3$, [22] could be present in the solution. An organic phase containing 99.5 mM HC302 and 15.8 mM Nd with an experimental $n_w = 3.52 \pm 0.26$ (the 48% theoretical capacity sample), could be composed of 4.3 ± 2.9 mM $\text{Nd}(\text{C302})_3$ and 5.8 ± 1.4 mM $\text{Nd}_2(\text{C302})_6$. An organic phase containing 99.5 mM HC302 and 29.8 mM Nd with an experimental $n_w = 5.34 \pm 0.40$ (the 90% theoretical capacity sample), could be composed of 2.8 ± 4.4 mM $\text{Nd}(\text{C302})_3$ and 13.5 ± 2.2 mM $\text{Nd}_2(\text{C302})_6$. By itself, the SANS data does not offer guidance in selecting between a $\text{Nd}_2(\text{C302})_6$ only model or one that includes $\text{Nd}(\text{C302})_3$ and $\text{Nd}_2(\text{C302})_6$, but the absorption spectra are useful here. If the absorption spectra of $\text{Nd}(\text{C302})_3$ and $\text{Nd}_2(\text{C302})_6$ are different, which is likely since the absorption spectra of $\text{Nd}(\text{C301})_3$ and $\text{Nd}_2(\text{C301})_6$ are clearly different, the change in Nd speciation that would be caused by increasing the Nd loading when multiple Nd species are present would give the two solutions different absorption spectra. The visible absorption spectra of the Nd containing HC302 solutions are identical within the experimental uncertainty in the Nd concentration.[20] The equivalence of the Nd-HC302 spectra is a strong indication that the relative concentration of the Nd species is the same in both solutions, and, as a consequence, that $\text{Nd}_2(\text{C302})_6$ is the only significant species in both solutions.

The absorption spectra of the Nd complexes with the dioxo ligands HDEHP and HC272 support and extend the findings of the SANS measurements. In the 0.10 M HDEHP solutions, a precipitate began to form when the Nd loading exceeded ca. 40% of the theoretical Nd capacity of the extractant with a 1:3 Nd:L ratio. Precipitation began at much lower Nd loadings (8% theoretical capacity) for the Nd containing solutions of the phosphinic acid extractant, HC272. Despite the difference in the loading capacities of the two extractants, the absorption spectra of the $\text{Nd}_2(\text{DEHP})_6$ solution at 33% Nd loading and the Nd-HC272 solution at 8% Nd loading are indistinguishable (Fig. 3). This demonstrates that the Nd-HC272 complex has the same stoichiometry and coordination geometry as the HDEHP complex, $\text{Nd}_2(\text{C272})_6$, even though the absolute Nd loading is significantly lower in the HC272 solution. The spectra in Fig. 3 also show that a different complex with different oscillator strengths, presumably the mononuclear $\text{Nd}[\text{H}(\text{DEHP})_2]_3$ or $\text{Nd}(\text{DEHP})_3$ complexes

observed at low metal loadings,[29, 30] predominates at high HDEHP concentrations and low (3%) Nd loading. The precise conditions of the formation of the 2:6 Nd:L complexes of dialkylphosphoric and dialkylphosphinic acid extractants is not a simple function of the metal loading. The mechanisms that affect the relative solubility of the complexes in the organic phase, like the nature of the alkyl groups and the extractant basicity, also appear to affect the formation of small oligomeric species, with the less soluble complexes forming oligomers at lower metal loadings. The Nd₂L₆ complexes that are observed for each of the ligands near Nd loadings that cause precipitate formation seem to be a discrete step from mononuclear complexes, like NdL₃, to neutral polymeric species with a metal:ligand ratio of n:3n that eventually become insoluble in the organic solvent.

5. ACKNOWLEDGEMENTS

The authors thank P. G. Rickert for purifying the extractants and D. Huff and S. Lopykinski of the Argonne Analytical Chemistry Laboratory for the ICP-AES determinations. This work was performed under the auspices of the Office of Basic Energy Sciences, Divisions of Material Science (for the SANS measurements made at the Intense Pulsed Neutron Source) and Chemical Sciences, U. S. Department of Energy under contract number W-31-109-ENG-38.

6. REFERENCES

- [1] T. Sekine and Y. Hasegawa, "Solvent Extraction Chemistry", Marcel Dekker, New York (1977).
- [2] T. Takahashi, Y. Suzuki and A. Yamasaki, "Solvent Extraction 1990: Proceedings of the International Conference on Solvent Extraction (ISEC'90)", Kyoto, Japan, Ed. By T. Sekine, Elsevier, New York, 189-193 (1992).
- [3] Y. A. Barbanel and N. K. Mikhailova, Russ. J. Inorg. Chem., 18, 365-368 (1973).
- [4] J. V. Beitz and J. C. Sullivan, J. Less-Common Met., 148, 159-166 (1989).
- [5] V. G. Lebedev, K. K. Palkina, S. I. Maksimova, E. N. Lebedeva and O. V. Galaktionova, Russ. J. Inorg. Chem., 27, 1689-1690 (1982).
- [6] D. N. Suglobov, Y. I. Trifonov, E. K. Legin and A. G. Tutov, J. Alloys Compd., 213-214, 523-527 (1994).
- [7] A. Tomita, T. Kanki, T. Asano and N. Sano, J. Chem. Eng. Japan, 33, 661-664 (2000).
- [8] Y. Zhu, J. Chen and R. Jiao, Solvent Extr. Ion Exch., 14, 61-68 (1996).
- [9] Y. Zhu, J. Xu, J. Chen and Y. Chen, J. Alloys Compd., 271-273, 742-745 (1998).
- [10] G. Modolo and R. Odoj, J. Alloys Compounds, 271-273, 248-281 (1998).
- [11] C. Hill, C. Madic, P. Baron, M. Ozawa and Y. Tanaka, J. Alloys Compd., 271-273, 159-162 (1998).
- [12] H. Hoshi, A. Tsuyoshi and K. Akiba, J. Radioanal. Nucl. Chem., 243, 621-624 (2000).
- [13] Y. Zhu and R. Jiao, Radiochim. Acta, 69, 191-193 (1995).
- [14] D. Li, A. Luo, C. Wang and M. Yuan, "Value Adding Through Solvent Extraction: Proceedings of the International Solvent Extraction Conference (ISEC'96)", Melbourne, Australia, Ed. by D. C. Shallcross, R. Paimin and L. M. Prvcic, University of Melbourne, Melbourne, 165-170 (1996).
- [15] K. C. Sole and J. B. Hiskey, Hydrometallurgy, 30, 345-365 (1992).
- [16] J. A. Partridge and R. C. Jensen, J. Inorg. Nucl. Chem., 31, 2587-2589 (1969).
- [17] P. Thiagarajan, H. Diamond, P. R. Danesi and E. P. Horwitz, Inorg. Chem., 26, 4209-4212 (1987).

- [18] R. Chiarizia, V. Urban, P. Thiyagarajan and A. W. Herlinger, *Solvent Extr. Ion Exch.*, 16, 1257-1278 (1998).
- [19] R. Chiarizia, V. Urban, P. Thiyagarajan, A. H. Bond and M. L. Dietz, *Solvent Extr. Ion Exch.*, 18, 451-478 (2000).
- [20] M. P. Jensen, R. Chiarizia and V. Urban, *Solvent Extr. Ion Exch.*, 19(5), in press (2001).
- [21] A. Guinier and G. Fournet, "Small Angle Scattering of X-rays", John-Wiley and Sons, New York (1955).
- [22] M. P. Jensen and A. H. Bond, *Radiochim. Acta*, submitted.
- [23] G. Allen and R. O. Colclough, *J. Chem. Soc.*, 3912-3915 (1957).
- [24] A. A. Pinkerton, Y. Meseri and C. Rieder, *J. Chem. Soc. Dalton Trans.*, 85-90 (1978).
- [25] M. Calligaris, A. Ciana, S. Meriani, G. Nardin, L. Randaccio and A. Ripamonti, *J. Chem. Soc. A*, 3386-3392 (1970).
- [26] G. Svensson and J. Albertsson, *Acta Chem. Scand.*, 45, 820-827 (1991).
- [27] K. M. Mühl siepen and R. Mattes, *Z. Anorg. Allg. Chem.*, 506, 115-124 (1983).
- [28] K. M. Mühl siepen and R. Mattes, *Z. Anorg. Allg. Chem.*, 506, 125-132 (1983).
- [29] J. M. Sánchez, M. Hidalgo, V. Salvadó and M. Valiente, *Solv. Extr. Ion Exch.*, 17, 455-474 (1999).
- [30] D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, *J. Inorg. Nucl. Chem.*, 4, 334-343 (1957).